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(54) Title: **LIQUID ABRASIVE CLEANING COMPOSITIONS**

(57) Abstract: The invention concerns aqueous liquid abrasive cleaning compositions comprising a 10-95% of a solid abrasive and 0.05-0.70% of an anionic thickening polymer and not more than 1.0% surfactant. The cleaning compositions may be in concentrated form containing 45% abrasive or more, which can be used as such or on dilution yield a ready to use abrasive composition. Alternatively they may be in a ready to use form containing 55% or less abrasive.



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LIQUID ABRASIVE CLEANING COMPOSITIONS

5 Field of the invention

The invention relates to aqueous liquid compositions which include an abrasive and a polymeric thickening agent to keep the abrasive suspended in the liquid.

10

Background of the invention

Liquid abrasive cleaning compositions are well known in the art and typically comprise a combination of detergent
15 surfactants, particularly anionic and nonionic surfactants, which together form a lamellar micelle phase and thereby cause thickening of the liquid. The lamellar phase acts as a suspending system to keep the solid abrasive in a stable suspension. Often an electrolyte is added to further
20 improve the stability of the suspension.

However, the detergent surfactants are expensive components and it is not always clear whether apart from their thickening and suspending action they really add to the
25 cleaning efficiency of the compositions. Therefore various attempts have been made to reduce the amount of surfactant and to provide the thickening and suspending power necessary to keep the abrasive in stable suspension by the addition of polymeric thickeners.

30

Thus, in WO 91/08283 liquid abrasive cleaning compositions are disclosed comprising 0.02-20% of detergent, 1-70% of particulate abrasive and 0.01-10% of a thickening mixture consisting of a linear non-starch type polymer and a
5 branched starch type polymer (amylopectin). The non-starch type polymers include various natural gums and synthetic polymers. Partially acetylated xanthan is particularly preferred. In practice the required amounts of thickening mixture are around 3% by weight of the total composition
10 and the examples all specify 1.5% of non-ionic surfactant.

In WO 95/08619 liquid abrasive cleaning compositions are disclosed comprising a cross-linked polyacrylate, either at least one non-ionic surfactant or a combination of an
15 anionic surfactant and a nonionic surfactant, a pH adjusting agent, and a calcium carbonate abrasive. The compositions are said to contain 0.1-2% of polyacrylate, 0.1-10% of nonionic, up to 10% anionic and 5-60% abrasive. In practice, according to the examples they contain 0.25-
20 0.4% polymer, 0.5% or more nonionic and 40% abrasive. The nonionic is required to provide the right viscosity characteristics. Similar compositions are disclosed in EP 649898 with the extra proviso that they contain hypochlorite and that the surfactant is bleach-stable.
25

In WO 96/35771 liquid abrasive cleaning compositions are disclosed comprising 10-30% of inorganic abrasive and a thickening system which consists of at least a cross-linked polyacrylate polymer and a smectite-type clay whereby the
30 latter preferably forms about 50-80% of the thickening

system. The thickening system preferably comprises 1-2.5% of the composition. In practice the cleaning compositions all contain at least 0.5 of polyacrylate and at least 0.75% of clay.

5

EP 0 352 358 describes suspensions of very fine silica based powders, such as zeolites, comprising organic polymeric compounds with hydroxylic groups and a molecular weight above 1500 as suspending agents and requiring the presence of certain cationic or zwitterionic surfactants as stabilizers. The particle size of the zeolites to be suspended is generally between 0.5 and 10 μm , with the bulk of the material having a particle size below 6 μm . The only polymers exemplified are combinations of guar and xanthan

15 gums.

In EP-A-0 875 557 an aqueous thickener composition suitable for a variety of end applications is described which comprises 0.04-30% w/w of a mixture of at least two surfactants in a specific ratio and with a difference in HLB of at least 1 unit and 0.01-5% w/w of an associative thickener selected from hydrophobically modified hydroxyethylcellulose, hydrophobically modified nonionic polyol and hydrophobically modified alkali-soluble emulsion polymer. In practice the amount of associative thickener is

25 1-2% and the amount of surfactant mixture 1-10%.

EP 0 301 885 discloses liquid abrasive cleaning compositions comprising up to 70% of abrasive, an aqueous suspending medium made of a combination of anionic

30

surfactants and electrolyte and also comprising a polyacrylate material having a molecular weight of between 500 and 3000. The compositions in practice contain at least 3.5% of surfactant.

5

Liquid abrasive cleaning compositions are normally sold in a ready to use form which contains 10-50%, generally 20-45% solid abrasive. Such compositions cannot be diluted to e.g. 10-20% solid abrasive content without losing their
10 stability leading to sedimentation. Although in the patent literature abrasive contents of up to 70% are quoted, such contents are not normally found in commercial products.

Brief description of the invention

15

It is an object of the present invention to provide stable aqueous liquid abrasive cleaning compositions which do not require detergent surfactant to obtain a stable suspension.

20 It is a further object of the invention to provide liquid aqueous abrasive cleaning compositions in which the abrasive is suspended with a polymeric thickening agent.

It is still a further object of the invention to provide
25 aqueous abrasive cleaning compositions which may be provided either in ready-to-use form, or in a concentrated form to be diluted by the consumer to a ready to use product without losing long term stability.

Accordingly, the invention provides liquid aqueous abrasive cleaning compositions comprising an insoluble abrasive and an anionic thickening polymer.

5 Detailed description of the invention

All percentages given herein are by weight and based on the total composition unless specified otherwise. The term "liquid" as used herein refers to products which are easily
10 pourable, as well as to products which are thick, almost paste-like, but because of their flow properties can physically still be classified as liquids

The aqueous liquid abrasive cleaning compositions according
15 to the invention comprise 10-95% of a solid abrasive, 0.05-0.70% of an anionic thickening polymer and not more than 1.0% of surfactant.

A dispersed, suspended solid particulate abrasive is an
20 essential ingredient of the liquid abrasive compositions according to the present invention. Preferably the amount of abrasive is at least 20% and for practical purposes generally not more than 80%, more preferably at most 75%.

25 The products may be formulated and packaged as ready-to-use compositions having an abrasives content as specified above. Such compositions may have the form of thick, viscous, almost paste-like products, or they may have the form of easily pourable liquids, which can easily be dispensed from
30 a bottle with a relatively narrow opening and are similar in

appearance to the products presently well known in the trade as "liquid abrasive cleaners". The thick-viscous type of ready-to-use products preferably have a high abrasives content of at least 45%, more preferably more than 50%, even 5 more preferably at least 55%, most preferably at least 60%. The pourable liquid type of ready-to-use compositions, on the other hand, preferably have a low abrasives content i.e. below 55%, more preferably 50% or less, even more preferably at most 45%.

10

Alternatively the compositions of the invention may be formulated and packaged as concentrates which are diluted before use by the addition of a suitable amount of water. Such compositions have the advantage that they require 15 smaller packaging for the same ultimate amount of ready-to-use product and thus provide an advantage in storage and transport. They may be prepared and transported in bulk as intermediates to a production facility close to the consumers where they are diluted with water and then 20 packaged and sold as ready-to-use products. On the other hand, they may also be packaged directly and sold as concentrates, to be diluted with water by the consumer at home.

These products also have a high abrasives content of 25 preferably at least 45%, more preferably more than 50%, even more preferably at least 55%, most preferably at least 60%.

Preferred abrasives have a Moh hardness of below 6, but above 1, although higher hardness abrasives can be employed

for specialist applications. Preferably the hardness is at least 2.

Suitable abrasives can be selected from inorganic abrasives such as zeolites, silicas, silicates, carbonates, aluminas, and organic polymeric abrasives such as polyethylene, polycarbonate, polyurethane, polystyrene, polypropylene, polyethylene terephthalate, polymethylmethacrylate and nylon, and mixtures thereof. Preferred abrasives are: calcium carbonate (as calcite), mixtures of calcium and magnesium carbonates (as dolomite), zeolite, alumina, hydrated alumina, feldspar, talc and silica. Calcite and dolomite and mixtures thereof with lower amounts of silica, especially amorphous silica, are particularly preferred due to their low cost and good abrasive properties.

Preferred weight average particle sizes for the abrasives fall in the range 0.5-500 microns, with values of 10-100 microns being particularly preferred. In this range an acceptable compromise between good cleaning behaviour and low substrate damage is achieved. Nevertheless, for silica to be used in combination with calcite or dolomite an average particle size in the range of 100-500 microns is very suitable as well.

25

The anionic polymers are used for obtaining a stable suspension of the abrasive particles in the aqueous medium. They are available in various forms and from many suppliers, e.g. as aqueous suspensions or in solid powdered form. Furthermore, they may be hydrophobically modified

30

and/or cross-linked. For "high abrasives content" products, i.e. products in which the amount of abrasive is at least 45%, more preferably more than 50%, even more preferably at least 55%, most preferably at least 60%, the
5 polymers are preferably used in an amount of at least 0.07%, more preferably at least 0.10, most preferably 0.15% or more. For those products the maximum level of polymers generally does not exceed 0.65% and is preferably at or below 0.60, more preferably less than 0.50 or even 0.45%,
10 most preferably below 0.40 or even 0.35%.

For the easily pourable ready-to-use products, on the other hand, the amount of polymer is preferably at least 0.07% and more preferably at least 0.10%, with maximum levels preferably being less than 0.50%, more preferably at most
15 0.40% or even 0.35%, most preferably at or below 0.30 or even 0.25%.

Suitable polymers are high molecular weight products , i.e. having a molecular weight of at least 10,000, particularly
20 at least 50,000 or even 100,000. Suitable polymers are to be found among the polycarboxylate type polymers, such as various polyacrylate homopolymers and copolymers which generally have a molecular weight of 500,000 or more, often well over 1000,000, and various polysaccharides, such as
25 carboxy-methylcelluloses, hydroxyethyl cellulose, hydroxypropyl-methylcellulose, carrageen, alginate, tragacanth gum, locust bean gum, guar gum, xanthan gum.

Very suitable are synthetic polycarboxylate polymers e.g.
30 hydrophobically modified emulsion polymers and carbomers

(solid powdered polyacrylic acids). The former are particularly useful for the "low abrasives content" products, while the latter are particularly useful for the "high abrasives content" products. suitable hydrophobically
5 modified emulsion polymers should preferably have η_0 of at least 1000 Pa.s.

(determined at 0.5% solution in water also containing 0.4% Genaminox CSL™ (TM for amine oxide marketed by Clariant), for meaning of η_0 : see below).

10

Suitable polymers include:

ACUSOL HASE and ASE series such as 820 and 842;

POLYGEL/NEUTRAGEL series such as W30, DA, DS, DR and DB;

RHEOVIS series such as CRX

15 CARBOPOL series such as Aqua 30, ETD 2690, ETD 2691, ETD 2623, EZ-1, EZ-2, EP-1, LNP-3, 663, 664, 674, 674, 1610, 1621, 1622 and 1623;

PEMULEN Series such as TR1 and TR2;

STRUCTURE 2001, 3001;

20 ALCOGUM SL-70 and SL-78.

ACUSOL is a trademark of Rohm & Haas;

CARBOPOL and PEMULEN are trademarks of B F Goodrich;

POLYGEL and NEUTRAGEL are trademarks of Sigma 3V;

25 RHEOVIS is a trademark of Ciba Specialities;

STRUCTURE is a trademark of National Starch & Chemical Co.;

ALCOGUM is a trademark of Alco.

Some of these thickening polymers, such as Carbopol ETD-
30 2690, loose their thickening properties in the presence of

an appreciable amount of calcium ions. Therefore, when calcite or a similar Ca containing abrasive is used, care should be taken to use a thickening polymer which is not Ca sensitive (such as Carbopol 674).

5

Other thickening agents, such as thickening clays or thickening silica are not necessary to achieve the required suspension stability and preferred embodiments of the invention do not contain such thickeners.

10

As outlined above, no surfactant is needed in the compositions according to the invention for stability reasons. Nevertheless it may be useful to add a limited amount of detergent surfactant to improve the cleaning
15 properties of the products on certain types of soils and/or to give foaming during use which is desired by some consumers. Nonionic, anionic, zwitterionic and amphoteric surfactants may be used. Nonionic surfactants are preferred. Nonionic surfactants may be combined with other classes of
20 surfactants, particularly with anionic surfactants. Generally, the presence of zwitterionic or cationic surfactants, although possible, does not serve any useful purpose and compositions without such surfactants are a preferred embodiment of the invention.

25

Suitable nonionic surfactants can be broadly described as compounds produced by the condensation of alkylene oxides which are hydrophilic with an organic hydrophobic compound which may be aliphatic or alkylaromatic. The length of the
30 hydrophilic polyalkyleneoxy group which is condensed with

any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

5 Particular examples include the condensation product of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut oil ethylene oxide condensate having from 2 to 15 moles of ethylene oxide per
10 mole of coconut alcohol; condensates of alkylphenols whose alkyl group contains from 6 to 12 carbon atoms with 5 to 25 moles of ethylene oxide per mole of alkylphenol; condensates of the reaction product of ethylenediamine and propylene oxide with ethylene oxide, the condensate
15 containing from 40 to 80% of ethyleneoxy groups by weight and having a molecular weight of from 5,000 to 11,000; tertiary amine oxides of structure R_3NO , where one group R is an alkyl group of 8 to 18 carbon atoms and the others are each methyl, ethyl or hydroxyethyl groups, for instance
20 dimethyldodecylamine oxide; tertiary phosphine oxides of structure R_3PO , where one group R is an alkyl group of from 10 to 18 carbon atoms, and the others are each alkyl or hydroxyalkyl groups of 1 to 3 carbon atoms, for instance dimethyldodecylphosphine oxide; and dialkyl sulphoxides of
25 structure R_2SO where the group R is an alkyl group of from 10 to 18 carbon atoms and the other is methyl or ethyl, for instance methyltetradecyl sulphoxide; fatty acid alkylolamides; alkylene oxide condensates of fatty acid
alkylolamides and alkyl mercaptans. The nonionic can also
30 be selected from a range of alkyl polyglycosides.

Particularly suitable are the ethoxylated aliphatic alcohol surfactants, such as C9-C11 5EO, C12-C13 6.5EO and C13-C15 7EO (EO numbers are averages), and the tertiary amine oxides
5 such as dimethyldodecylamine oxide and dimethyldecylamine oxide or amine oxide mixtures containing a large proportion of these.

Suitable anionic surfactants are water-soluble salts of
10 organic sulphuric acid esters and of sulphonic acids which have in the molecular structure an alkyl group containing 6-22 C-atoms. They are usefully added to provide the compositions with good foaming properties, which are often considered desirable by the consumer.

15

Examples of such anionic surfactants are water soluble salts of:

- long chain (i.e. 8-22 C-atom) alcohol sulphates (hereinafter referred to as PAS), especially those
20 obtained by sulphating the fatty alcohols produced by reducing the glycerides of tallow or coconut oil;
- alkyl benzene sulphonates, such as those in which the alkyl group contains from 6 to 20 carbon atoms;
- secondary alkanesulphonates (hereinafter referred to as
25 SAS).

Also suitable are salts of:

- alkyl glyceryl ether sulphates, especially those ethers
30 of the fatty alcohols derived from tallow and coconut oil;

- fatty acid monoglyceride sulphates;
- sulphates of the reaction product of one mole of a fatty alcohol and from 1 to 6 moles of ethylene oxide;
- salts of alkylphenol ethyleneoxy-ether sulphates with
5 from 1 to 8 ethyleneoxy units per molecule and in which the alkyl groups contain from 4 to 14 carbon atoms; and mixtures thereof.

The preferred water-soluble synthetic anionic surfactants
10 are the sodium, potassium, magnesium and ammonium salts of alkyl-benzenesulphonates, olefinsulphonates and alkyl sulphates, and the fatty acid mono-glyceride sulphates.

Amphoteric surfactants that optionally can be employed are
15 derivatives of aliphatic secondary and tertiary amines containing an alkyl group of 8 to 18 carbon atoms and an aliphatic group substituted by an anionic water-solubilising group, for instance sodium 3-dodecylamino-propionate, sodium 3-dodecylaminopropane sulphonate and sodium N-2-
20 hydroxydodecyl-N-methyl taurate.

Further examples of suitable surfactants are compounds commonly used as surface-active agents mentioned in the well-known textbooks "Surface Active Agents", Volume I by
25 Schwartz and Perry and "Surface Active Agents and Detergents", Volume II by Schwartz, Perry and Berch.

The compositions according to the invention may contain a total amount of 0-1% of surfactant, preferably below 0.5%.
30 More preferably the total level of surfactant does not

exceed 0.4% or even 0.3%. For a useful increase in cleaning and/or foaming properties a minimum level of 0.01% of total surfactant is advisable, preferably at least 0.02%, more preferably at least 0.05%, or even 0.1%.

5

The level of nonionic surfactant should preferably be below 0.5%, more preferably be at or below 0.45% and most preferably at or below 0.35% or even 0.3%. To improve the cleaning properties of the composition as well as stability
10 of the suspension the level of nonionic is preferably at least 0.01%, more preferably at least 0.02%. For concentrated products the amount of nonionic is more preferably at least 0.02%, most preferably at least 0.03%.

15 The compositions according to the invention are alkaline, more particularly they have pH above 8, preferably 9 or higher. Thus the compositions can be made alkaline with use of a suitable base such as an alkali metal hydroxide or carbonate, ammonia or an organic base with pKa above 9 such
20 as triethylamine, amino-methylpropanol (AMP), aminobutanol, mono-, di- or tri-ethanolamine, monoisopropylamine or aminomethylpropanediol. AMP is particularly useful, and preferably if added in an amount of up to 0.5%, more preferably 0.2-0.4% in the absence of another base or 0.1-
25 0.2% in the presence of another base.

The compositions according to the invention generally do not need any extra electrolyte other than the possible anionic surfactant and the base for setting the pH. Preferably the

level of additional electrolyte is below 0.3%, more preferably below 0.2%.

Optional components

5

The abrasive compositions according to the invention may contain optional components which improve their cleaning properties such as organic solvents known in the art for use in abrasive cleaning compositions, particularly solvents of
10 which the molecules bear a polar group, such as hexanol, ethylene- and propylene glycol alkyl ethers. They may also contain bleaching agents, particularly halogen bleaching agents, more particularly hypochlorite provided that hypochlorite stable polymers and surfactants are used.

15

Furthermore they may contain additional components such as:

- components to further increase their attraction to the consumer, such as colorants, optical brighteners and particularly perfumes (perfumes may have a further
20 positive influence on the stability of the suspension);
- preservatives to prevent microbial contamination.

Liquid properties

25 Satisfactory "low abrasives content" ready-to-use liquid abrasive cleaning compositions according to the invention have such fluid flow characteristics that they are stable suspensions when not in use, but thin enough to pour the liquid from the packaging container and spread it on the
30 soiled surface without appearing thin and watery. Thus the

liquid product preferably has the following liquid flow properties:

η_0 is at least 1500 Pa.s

5 σ_c is 2.5-25

η_{21} is at least 0.1 Pa.s

Wherein: η_0 is the viscosity at zero shear rate (determined by extrapolation); σ_c is the shear stress at which the
10 viscosity is $0.1 \cdot \eta_0$; and η_{21} is the viscosity at a shear rate of 21 s^{-1} .

Preferably η_0 is at least 2000Pa.s, more preferably at least 2500.

Preferably η_{21} is 0.3-5.0, more preferably 0.6-1.8, most
15 preferably 1.0-1.5 Pa.s.

Measurements made on:

CSL 100 (TA Instruments) with vane and basket measuring system (basket internal diameter 48mm, vane diameter 38mm
20 and height 24.5mm) to measure viscosity from a stress (σ) of 0.01 Pa to the stress required to give a shear rate of 1 s^{-1} ;

Haake RV20 with M5 measuring head and SV2p measuring geometry to measure viscosity between shear rates of 0.1 and
25 389 s^{-1} . All measurements made at 20°C .

Satisfactory "high abrasives content" concentrated liquid abrasive cleaning compositions are liquids or pastes which

are suitable for dilution with water to 1.2-4 times,
preferably 1.5-3 times, more preferably 2-3 times the
original volume, thereby producing a stable ready-to-use
liquid abrasive cleaning composition, preferably a cleaning
5 composition with the liquid flow properties specified above.

Satisfactory "high abrasives content" ready-to-use liquid
abrasive cleaning compositions are generally viscous, or
almost paste-like liquids. Although they do not generally
10 spread easily when put on a surface, they do obtain a smooth
and "undisturbed" surface again when left alone for a few
minutes to a few hours in the container. Such products are
preferably not packaged in a container from which they have
to be dispensed by pouring, however, containers such as a
15 tub or tin, from which suitable amounts can be taken out on
a suitable applicator such as a wet cloth or sponge, or
containers from which they can be dispensed by squeezing,
such as a tube, are very useful.

20

Preparation

The compositions according to the invention may simply be
prepared by mixing the various components. It is preferred
25 to first make a dilute (e.g. 1-2%) aqueous solution or
dispersion of the polymer and then mix in the other
components subsequently. The other components may be first
made into a slurry with the remaining amount of water after
which the solution (dispersion) and the slurry are mixed.
30 Sometimes it is advantageous to neutralize the aqueous

polymer solution with part of the base before mixing it with the other components.

EXAMPLES

5

Examples 1-4

Liquid abrasive cleaning compositions according to the Examples 1-4 in Table I below were prepared.

10

Table I

Ingredients	Percentage level			
	1	2	3	4
NEODOL 135-7E ¹⁾	0.08	0.08	0.13	0.12
Calcite	35.00	45.00	57.36	70.13
ACUSOL 820	0.26	0.26	0.43	0.41
NaOH	0.055	0.055	0.09	0.09
Perfume	0.30	0.30	0.49	0.47
Water	64.31	54.31	41.50	28.79
Total	100	100	100	100

¹⁾ C13-15 alcohol with (average) 7EO marketed by Shell

15

The compositions were prepared by first diluting the 30wt% ACUSOL solution to 1wt% and neutralising it with NaOH solution. The ACUSOL solution is stirred at room temperature until it appears homogeneous, while taking care that the

solution is not aerated. The remaining components and the remainder of the water of the formula are made into an aqueous slurry and the ACUSOL solution is carefully added while stirring. Stirring is continued until a homogeneous suspension is obtained, again taking care that aeration is avoided.

A composition identical to Example 1 was prepared by diluting a quantity of the composition of Example 3 with an equal volume of water followed by shaking or stirring. Likewise, a composition identical to Example 2 was prepared by diluting a quantity of Example 4 with an equal volume of water.

All six examples were tested for stability by storing samples of them for three months at 37°, 20° and 4°C. Other samples were taken through three freeze/thaw cycles. None of the samples showed any visible sedimentation.

20

Examples 5-6

Concentrated abrasive cleaning compositions having the composition described in Table II were prepared by making a 2% dispersion of the polymer in water and adding this, with stirring, to a slurry of calcite, surfactant, NaOH and perfume in the remaining amount of water. Stirring was continued until a homogeneous mixture was obtained.

The compositions could be diluted by adding an equal volume of water and shaking briefly, to obtain ready to use cleaning compositions containing 45% abrasive.

5

Ingredients	Table II	
	Percentage level	
	5	6
NEODOL 135-7E	0.13	0.13
Calcite	70.13	70.13
CARBOPOL 674	0.28	
POLYGEL DR		0.20
NaOH	0.09	0.09
Perfume	0.48	0.48
Water	28.89	28.97
Total	100	100

Samples of the concentrated as well as the diluted
10 compositions were stability tested as described for the
examples 1-4 and did not show any visible sedimentation.

Examples 7-13

15 High foaming ready-to-use abrasive cleaning compositions
were prepared having the compositions described in table III
below, made up to 100% with water.

Table III

Example	Polymer %	Amine Oxide %	Calcite %	AMP	Carbonate	NaOH
7	0.16	0.2	45	0.3	0	0
8	0.15	0.2	45	0.28	0	0
9	0.14	0.2	45	0.26	0	0
10	0.19	0.25	45	0	0.15	0.08
11	0.17	0.2	45	0.18	0	0.048
12	0.19	0.25	45	0.15	0	0.054
13	0.16	0.25	45	0.15	0	0.045

The polymer was Polygel DR, the amine oxide was Genaminox
 5 CSL, the calcite was Omyacarb 30. All examples additionally
 contained 0.4% perfume.

Example 14

10

A "high abrasives content" ready-to-use product was prepared
 having the composition described below:

Acusol 820	0.280%
15 Genaminox CSL	0.400%
Na hydroxyde	0.051%
Omyacarb 65	65.0 %
Proxel GXL (preservative)	0.016%
Water	to 100%

20

The product had pH 9.8 and a density of 1.8 g/cm^3 . It was stored in a tub from which it could easily be taken on a wet cloth to be applied to a surface to be cleaned. The surface of the product remaining in the tub restored its smooth and level appearance again after being left for half an hour.

CLAIMS

1. Aqueous liquid abrasive cleaning compositions comprising a solid abrasive and an anionic thickening polymer characterised in that the abrasive is present in an amount of 10-95% and the anionic polymer in an amount of 0.05-0.70% and the composition contains not more than 1.0% surfactant.
2. Compositions according claim 1 characterised in that the amount of abrasive is 20-80%
3. Compositions according to claims 1 or 2 characterised in that the abrasive is chosen from zeolites, silicas, silicates, carbonates, aluminas and organic polymeric abrasives.
4. Compositions according to claim 3 characterised in that the abrasive is chosen from calcium carbonate, mixtures of calcium and magnesium carbonates, zeolite, alumina, hydrated alumina, feldspar, talc and silica.
5. Compositions according to any one of claims 1-4 characterised in that the amount of anionic polymer is 0.07-0.50%.
6. Compositions according to any one of claims 1-5 characterised in that the anionic polymer is a polycarboxylate polymer chosen from polyacrylate

homopolymers, polyacrylate copolymers and polysaccharides.

7. Compositions according to any one of claims 1-6 characterised in that they contain less than 0.50% of surfactant.
8. Compositions according to claim 7 characterised in that they contain 0.01-0.45% of nonionic surfactant.
9. Compositions according claims 7-8 characterised in that they also contain anionic surfactant.
10. Compositions according to claims 1-9 characterised in that they have pH above 8.
11. Compositions according to any one of claims 1-4 characterized in that they contain at least 45% abrasive, 0.02-0.50% of surfactant and 0.07-0.60 of anionic polymer.
12. Compositions according to claim 11 characterized in that the content of abrasive is above 50%.
13. compositions according to any one of claims 1-4 characterised in that they contain at most 55% abrasive, 0.02-0.35% of surfactant and 0.07-0.35% of anionic polymer.

14. Compositions according to claim 13 characterized in that they contain at most 50% of abrasive.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/06592

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C11D17/00 C11D3/14 C11D3/37 C11D3/22 C11D3/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 649 898 A (CLOROX CO) 26 April 1995 (1995-04-26) claim 1; example I ----	1-10, 13, 14
X	WO 96 35771 A (RECKITT & COLMAN INC) 14 November 1996 (1996-11-14) page 7, line 5 - line 13; example 2 ----	1-6, 10
X	EP 0 352 358 A (AUSIDET SPA) 31 January 1990 (1990-01-31) page 7, line 2 - line 40; claim 1; examples ----	1-7, 11-14
A	EP 0 301 885 A (UNILEVER PLC ; UNILEVER NV (NL)) 1 February 1989 (1989-02-01) claims 1-8; example P ----- -/--	1-14

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

15 November 2000

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INTERNATIONAL SEARCH REPORT

Int. l. Application No

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>WO 95 08619 A (CLOROX CO) 30 March 1995 (1995-03-30) cited in the application claims 1-14; examples 1,2; table 3 -----</p>	1-14

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 00/06592

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0649898	A	26-04-1995	CA 2134062 A	23-04-1995
			US 5529711 A	25-06-1996
			US 5827810 A	27-10-1998
WO 9635771	A	14-11-1996	GB 2300643 A	13-11-1996
			AU 705220 B	20-05-1999
			AU 5853796 A	29-11-1996
			CA 2219679 A	14-11-1996
			GB 2315772 A,B	11-02-1998
			ZA 9603733 A	21-11-1996
EP 0352358	A	31-01-1990	US 5190693 A	02-03-1993
EP 0301885	A	01-02-1989	AU 608343 B	28-03-1991
			AU 2007888 A	02-02-1989
			BR 8803782 A	21-02-1989
			CA 1310562 A	24-11-1992
			DE 3866049 A	12-12-1991
			ES 2027764 T	16-06-1992
			JP 1087699 A	31-03-1989
			JP 1915554 C	23-03-1995
			JP 6043599 B	08-06-1994
			US 4911857 A	27-03-1990
			ZA 8805532 A	28-03-1990
WO 9508619	A	30-03-1995	US 5470499 A	28-11-1995
			CA 2165668 A	30-03-1995
			EP 0720646 A	10-07-1996
			US 5529711 A	25-06-1996
			US 5554321 A	10-09-1996
			US 5827810 A	27-10-1998